Studies on Temperature Dependent Birefringence and Molecular Orientations of Smectic-A and Smectic-C Phases

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Abstract: Two or more multi-component system of N-Cetyl-N, N, N, trimethly ammonium bromide (CTAB), Cetyl alcohol + Orthophosphoric acid (CA+H₃PO₄) exhibits an induced smectic phases, such as smectic-A, smectic-C and smectic-E phases sequentially when the specimen is cooled from its isotropic melt. These phases have been characterized by using DSC, Optical microscopic techniques and X-ray studies. The molecular tilt and birefringence have been discussed in the region of smetic-A and smectic-C phases respectively at different temperature.

Keywords: Birefringence, layer spacing, Molecular orientation, x-ray studies, Optical studies, Smectic Phases

1. Introduction

Liquid crystal compounds and mixtures are selected for applications in industrial technologies in accordance with their optical properties. Liquid crystals with a large optical anisotropy are required in displays with small cell thickness and small switching time. Substances that are not as an ordered, even though it has an ordered of crystalline solid and hence if they have some degree of alignment are properly called liquid crystals. Depending on the molecular orientation, liquid crystals may show number of specific structures, which means the transition from the solid state to the liquid isotropic state is not a single one, but a succession of transitions passing by several thermodynamically stable phases. The microscopic investigation is one of the most important tools for the identification and the interior classification of different liquid crystalline phases. The molecules of thermotropic liquid crystals are able to orient themselves with the long axis parallel to a certain direction. By consequence, they can exist in a series of different structures such as nematic, smectic, or cholesteric phases. Each of them is defined by some ordering particularities: the nematic phase has a molecular parallel ordering but the smectic phase has a planar parallel ordering and the structure is not stratified; the smectic phase has a planar stratified structure and the cholesteric phase has a helicoidal structure. The tendencies of liquid crystalline molecules are to be pointed out along the director, which leads to a condition known as anisotropy [1-4].

In the present work, our aim is to study the mixture of multi-component systems, namely: N-Cetyl-N, N, N, trimethly ammonium bromide (CTAB), Cetyl alcohol + Orthophosphoric acid (CA+H₃PO₄). Different concentrations of these mixtures show an induced smectic phases such as Smectic-A, Smectic-C and Smectic-E phases, sequentially when the specimen was cooled from its isotropic melt. The phase transition temperature for different concentrations of these mixtures was determined by using polarizing microscope in conjunction with hot stage. These phases have been characterized by using differential scanning calorimeteric (DSC) and X-ray diffraction technique. Temperature variation of optical anisotropy and intermolecular interactions of the given ternary molecules CTAB in (CA+H₃PO₄) have also been discussed.

2. Experimental Studies

In the present work we have been considered the compounds namely: N-Cetyl-N, N, N, trimethly ammonium bromide (CTAB), Cetyl alcohol (CA) and Orthophosphoric acid (H₃PO₄) was obtained from the Padmashri Scientific, Mysore-India. It was further purified twice by a recrystallization method using benzene as a solvent. For our experimental studies, the ternary system of given molecules CTAB in (CA+H₃PO₄), we have kept the concentration of CTAB 40% and the concentrations of CA and H₃PO₄ have been varied. Mixtures of different concentrations of CTAB in (CA+H₃PO₄) were prepared and were mixed thoroughly and these mixtures of various concentrations of CTAB in (CA + H₃PO₄) were kept in desiccators for a long time. The samples were subjected to several cycles of heating, stirring and centrifuging to ensure homogeneity. The phase transition temperatures of these concentrations were measured with the help of Gippon-Japan polarizing microscope in conjunction with a hot stage. The samples were sandwiched between the slide and cover slip and were sealed for microscopic observations. The phase transition temperatures were compared with the values obtained from DSC at the Raman Research Institute, Bangalore, India. XRD patterns were taken using a JEOL X-ray diffractometer to study the structural patterns of smectic phases [5-7]. The ¹H NMR spectroscopic studies were carried out using a Bruker 300-MHz NMR spectrometer at 299 K to understand the layer structure and inter molecular interactions of given ternary molecules. The density and refractive indices in the optical region are determined at different temperatures by employing the techniques described by the earlier investigators [8, 9].
3. Results and Discussions

Phase Diagram

The partial phase diagram of given molecules is a very important method to determine the structural formation and stability of liquid crystalline phase at different temperatures for different concentrations. The partial phase diagram in the present case is as shown in Figure 1. This clearly illustrates that, mixtures with the concentrations ranging from 15% to 55% of CTAB in (CA+H₃PO₄) exhibit an Smectic-A, Smectic-C and Smectic-E phases, sequentially when the specimen was cooled from its isotropic melt. DSC thermogram was taken for the mixture of 40% CTAB in (CA + H₃PO₄) as presented in Figure 2. DSC studies clearly show the phase transition temperature of the given materials by detecting the change in enthalpy associated with the first / second order transition. Even though the precise identity of the phase cannot be obtained, but the level of enthalpy change at the phase transition does provide some identification of the types of phase involved. If the entropy at phase transition shows a discontinuity, then a discontinuous first order transition has occurred [10-13]. From DSC thermogram, the sequential representation of liquid crystalline phases for the sample of 40% CTAB in (CA + H₃PO₄) is as follows.

Iso121°C → SmA 104°C → SmC 78°C → SmE 66°C → Below 66°C Cryst

Optical Texture Studies

For the purpose of optical texture studies, the sample was sandwiched between the slide and cover glass, and then the optical textures were observed using Gippon-Japan polarizing microscope in conjunction with hot stage. The concentrations of mixture ranges from 10% to 60% are slowly cooled from its isotropic melt, the genesis of nucleation at several points which appear as minute bubbles initially, but which progressively grow radially and form a focal conic fan texture of smectic-A phase in which the molecules are arranged in layers and the texture is shown in Figure 3(a). Focal conic textures are particularly useful for identifying mesophase and hence this phase appears to be meta-stable: it undergoes slow transformations to give schlieren texture of smectic-C phase as shown in Figure 3(b), on cooling the specimen. A smectic-C phase that occurs below a smectic-A phase is obvious. Because the transition is not sharp as many mesophase transitions and it is due to the presence of a temperature dependent tilt angle. Fan texture will continue to changes the tilt angle: that changes the obtained fan texture are more muddied and less fan looking and it shows the changes are more obvious which are the characteristics of schlieren texture, which shows a wave after wave of alternating light and dark gray texture. Sequentially once again on further cooling the schlieren texture of smectic-C phase, the phase becomes more fluid and a scintillation type of effect occurs due the fluctuations of smectic-C phase. This scintillation is rarely observed in any other mesophase. The appearance of focal conic fan textures are radially striated [14, 15], which are the characteristics of smectic-E phase and it is observed, which as shown in Figure 3(c). The appearance of arcs across the backs of the fan in smectic-E phase is slowly disappearing to form a crystalline phase towards at room temperature. Here it can be noticed that: in the present study, the phase transition temperatures of polymorphic smectic modifications have been observed, which are different from the values were observed in a similar type of studies by T. N. Govindiah et al.[16, 17], and in which the mixture of a different compound with organic solvents has been studied. Hence, the interaction of organic solvents looks to be different with different compounds.

X-Ray Studies

To understand the change in layer spacing’s in smectic-A and smectic-C phases with respect to temperature, X-ray diffractometer traces were taken. The traces obtained for the mixture of 40% CTAB in (CA + H₃PO₄) at different temperatures correspond to smectic-A and smectic-C phases. It is observed that as the temperature increases the layer spacing also increases in smectic-C phase. But in smectic-A phase, the layer spacing’s are almost constant and correspond these variations are shown in Figure 4 [18, 19]. Here it is pertinent to remark that, the smectic-C phase has a layered structure in which the smectic layer normal and the director are no longer collinear. At the smectic-A to smectic-C transition molecules start to tilt with respect to the layer normal and layer spacing’s are decreases correspondingly. The molecular tilt is the order parameter for the smectic-C phase. Molecular orientations are the better understanding of molecular tilt and the phase transition.

1H-NMR and IR Studies

The 1H NMR spectrum of N-Cetyl-N, N, tri-metyl ammonium bromide, Cetyl alcohol and orthophosphoric acid of the given mixture shows a triplet peak at δ 3.6 due to presence of CH₃, and a singlet at δ 1.35 indicating the presence of -N-(CH₃)₃, a tertiary amine. The absence of OH peak around δ 2.3 indicates the present multi component system. It was further confirmed by IR spectroscopy. The IR peak at 3450 Cm⁻¹ due to the presence of OH in Cetyl alcohol is missing in the present mixture [20].

Optical Anisotropic Studies On Molecular Dynamics

Molecular layer spacing’s as function of temperature dependent birefringence of different liquid crystalline phases for the sample of 40% CTAB in (CA + H₃PO₄) as shown in Figures 5. Which explains the relations between the wavelength of optical textures, molecular layer spacing’s and birefringence of the given molecules are studied in the region of smectic-A and smectic-C pahses respectively at different temperature. A number of significant observations are emerged from this study and then here we have observed the reactive mesogens are approaches a successful in forming molecular layers with desirable transport properties available across the temperature range between smectic-A and smectic-C phases. Remarkably it shows the values of birefringence increases for a given mixture at certain wavelengths of optical textures of molecular tilt with respect to the layer spacing’s are increases. The phenomenon of changes in birefringence with temperatures for the liquid crystalline materials makes it possible to be used as a thermometer in this region of temperature and displays the
temperature of its environment by the reflected color. It is also can be used to create sensors with a wide variety of responses to the temperature change. When the solid material is solidified at room temperature, it has a white color with different phases of aggregations. When the given sample was placed polarizing microscope and the optical textures have been observed. The bright and dark areas are the resultant intensity distribution of the samples due to interference of polarized light. Different colors which are viewed between crossed polarizer correspond also to different twist states[21].

4. Conclusions

In light of the above results, we have drawn the following conclusions. The multi-component system of given molecules exhibits an conventional smectic phases showing the formation of smectic-A, smectic-C and smectic-E phases respectively at different concentrations. Intermolecular interactions of given multi-component system has been discussed. The variations of molecular tilt and birefringence have also been discussed in the region of smectic-A and smectic-C phases respectively at different temperatures.

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References


Figure Captions

Figure 1: Partial phase diagram for the mixture of CTAB in (CA + H3PO4).

Figure 2: DSC thermogram for the sample of 40 % of CTAB in (CA + H3PO4).

Figure 3: Microphotographs obtained in between the crossed polars,

a) Focal conic fan shaped texture of SmA phase (250X).
b) Schlieren texture of SmC phase (250X).
c) Radial stirration of SmE phase (250X).

Figure 4: Variation of layer spacing with temperature for the sample of 40 % of CTAB in (CA+H3PO4).

Figure 5: Variation molecular layer spacing’s as function of temperature dependent birefringence for the sample of 40 % of CTAB in (CA+H3PO4).
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